



## 1,5-Dipolar electrocyclizations in reactions of alpha-Thioxo Ketones and alpha-Thioxo Thioamides with Diazo compounds

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**Abstract:** Several reactions of  $\alpha$ -thioxo ketones and  $\alpha$ -thioxo thioamides with diazo compounds were investigated. Most of them proceeded via a reactive thiocarbonyl ylide, which underwent a [2+3] cycloaddition with the  $\alpha$ -thioxo ketone to give the 'Schönberg products' 17–19 or a 1,5-dipolar electrocyclization to give the corresponding five membered 1,3-oxathioles (i.e., 13, 20a, 20b, 21, and 25) and 1,3-dithioles (i.e., 33, 34, and 35), respectively. In the case of thioamide 32, the thiocarbonyl ylides underwent a competitive 1,3-dipolar electrocyclization to yield the corresponding thiiranes. In these cases, spontaneous desulfurization led to the corresponding alkenes 36 and 37. The nature of the employed thiocarbonyl or diazo compounds seem to be decisive for the reaction pathway. When the diazo compound bears at least one H-atom in the  $\beta$ -position to the diazo group (i.e., diazocyclohexane 15f), no products of an electrocyclization could be isolated in the reactions with  $\alpha$ -thioxo ketones or  $\alpha$ -thioxo thioamides. The only products which were isolated in these cases were 2-[(cyclohex-1-enyl)sulfanyl]-1,2-diphenylethanone (22) and 2-[(cyclohex-1-enyl)sulfanyl]-N,N-dimethyl-2-phenylthioacetamide (38), which were formed by a [1,4]-H shift of the corresponding thiocarbonyl ylides.

DOI: <https://doi.org/10.1002/hlca.200690182>

Posted at the Zurich Open Repository and Archive, University of Zurich

ZORA URL: <https://doi.org/10.5167/uzh-51285>

Journal Article

Accepted Version

Originally published at:

Egli, D H; Linden, Anthony; Heimgartner, H (2006). 1,5-Dipolar electrocyclizations in reactions of  $\alpha$ -Thioxo Ketones and  $\alpha$ -Thioxo Thioamides with Diazo compounds. *Helvetica Chimica Acta*, 89(9):1910-1926.

DOI: <https://doi.org/10.1002/hlca.200690182>

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## **1,5-Dipolar Electrocyclizations in Reactions of $\alpha$ -Thioxoketones and $\alpha$ -Thioxothioamides with Diazo Compounds**

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<sup>1</sup>) Part of the diploma work (2002) and the projected Ph.D. thesis of *D. H. E.*,  
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Several reactions of  $\alpha$ -thioxoketones and  $\alpha$ -thioxothioamides with diazo compounds were investigated. Most of them proceeded *via* a reactive thiocarbonyl ylide, which underwent a [2+3] cycloaddition with the  $\alpha$ -thioxoketone to give the 'Schönberg products' **17-19** or a 1,5-dipolar electrocyclization to give the corresponding five membered 1,3-oxathioles (**13**, **20a**, **20b**, **21**, **25**) and 1,3-dithioles (**33**, **34**, **35**), respectively. In the case of thioamide **32**, the thiocarbonyl ylides underwent a competitive 1,3-dipolar electrocyclization to yield the corresponding thiiranes. In these cases, spontaneous desulphurization led to the corresponding alkenes **36** and **37**.

The nature of the employed thiocarbonyl or diazo compounds seem to be decisive for the reaction pathway. When the diazo compound bears at least one H-atom in the  $\beta$ -position to the diazo group (*i.e.* diazocyclohexane **15f**), no products of an electrocyclization could be isolated in the reactions with  $\alpha$ -thioxoketones or  $\alpha$ -thioxothioamides. The only products which were isolated in these cases were 2-[(cyclohex-1-enyl)sulfanyl]-1,2-diphenylethanone (**22**) and 2-[(cyclohex-1-enyl)sulfanyl]-*N,N*-dimethyl-2-phenylthioacetamide (**38**), which were formed by a [1,4]-H shift of the corresponding thiocarbonyl ylides.

**1. Introduction.** – The reactions of thiocarbonyl compounds **1** with diazo alkanes **2a** have been investigated extensively over the last few years. Most of the reactions led to 1,3-dithiolanes **3a** and **3b** by 1,3-dipolar cycloaddition of the intermediate thiocarbonyl ylide **4** with the original C=S compound (the so called *Schönberg* reaction [1] [2]) or to thiiranes **5** by 1,3-dipolar electrocyclization. The latter form alkenes **6** by sulfur-extrusion [2-4] (*Scheme 1*). Many studies have attempted to determine the intermediates of these reactions. All results indicated the formation of thiocarbonyl ylides **4** as intermediates, which react *via* several pathways to form the products (for reviews see [5][6]). These intermediates could be intercepted by dipolarophiles to give the [2+3] adducts **7** in a 1,3-dipolar cycloaddition. This reaction led not only to the understanding of the reaction mechanism, but also opened new access to S-heterocycles.

*Scheme 1*

Another goal was the incorporation of the dipolarophile into the thiocarbonyl ylide, in order to promote a ring closure *via* 1,5-dipolar electrocyclization. These studies have shown that 1,3-oxathioles **8** can easily be prepared by generation of a thiocarbonyl ylid **9** *via* a Rh<sub>2</sub>(OAc)<sub>4</sub> or LiClO<sub>4</sub> catalyzed reaction of  $\alpha$ -diazocarbonyl compounds **10** with thiocarbonyl compounds **1**, followed by a 1,5-dipolar electrocyclization [7-9]. In a few cases, it was shown that **8** can also be prepared by the reaction of  $\alpha$ -thioxocarbonyl compounds **11** with diazo compounds **2b** by using Rh<sub>2</sub>(OAc)<sub>4</sub> as a catalyst [10][11]. This is not surprising, because the 2,5-dihydro-1,3,4-thiadiazole **12** is a common intermediate in both reactions (*Scheme 2*).

*Scheme 2*

The main target of the present study was to investigate further the scope and limitations of the 1,5-dipolar electrocyclization of thiocarbonyl ylids with a conjugated  $\pi$ -system and, in particular, the influence of this conjugated  $\pi$ -system in the thiocarbonyl compounds on the course of the reaction with diazo compounds.

## 2. Results and Discussion.

2.1. *Reactions with  $\alpha$ -Thioxocarbonyl Compounds.* As 1,2-diphenyl-2-thioxoethanone (**14**) reacted cleanly with diphenyldiazomethane (**15a**) to give 2,2,4,5-tetraphenyl-1,3-oxathiole (**13**) as the only product [11] (*Scheme 3*)<sup>2</sup>, **14** was selected as a suitable candidate for the reaction with phenyldiazomethane (**15b**), ethyl-2-diazoacetate (**15c**), and diazomethane (**15d**), respectively. It was expected that these reactions would lead to the corresponding 1,3-oxathioles by 1,5-dipolar electrocyclization of the intermediate thiocarbonyl ylide **16**. Unexpectedly, the products of the reaction in  $\text{CH}_2\text{Cl}_2$  at room temperature obtained after chromatography on  $\text{SiO}_2$  were not the expected ones. The main product in each case was a yellow stinky oil, which could not be analyzed because of decomposition. The results were the same when the reaction conditions were changed (low temperature, heating, catalysis with  $\text{Rh}_2(\text{OAc})_4$  or  $\text{LiClO}_4$ ). In each case, the corresponding racemic *Schönberg* product, *i.e.* **17-19**, was isolated as a minor product in 15 to 25% yield (*Scheme 3*).

### *Scheme 3*

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<sup>2</sup>) The repetition of the reaction reported in [11] yielded **13**, which was identical with the product obtained from the reaction of 2-diazo-1,2-diphenylethanone and thiobenzophenone [7].

The structures of **17-19** have been established by X-ray crystallography (*Fig. 1*). The five-membered ring of **17** has a half-chair conformation twisted on S(2)-C(3). The two benzoyl groups at C(2) and C(4) are *trans* oriented, and the configuration of the Ph groups at C(2), C(4) and C(5) is *trans, cis*. In **18**, the ethyl group of the ester side chain is disordered over two orientations that differ slightly by a twist about this O-Et bond. Two equally occupied positions were refined for the terminal methyl groups of this moiety. The five-membered ring has an envelope conformation with C(2) as the envelope flap. The two benzoyl groups at C(4) and C(5) are *cis* to the ester group and to each other. The five-membered ring of **19** has a half-chair conformation twisted on C(1)-S(5). The benzoyl substituents lie *trans* to each other.

It is remarkable that the regioselectivity of the formation of the dithiolane ring of **17** is different to that of **18** and **19**. Furthermore, the relative configuration of the benzoyl groups at C(4) and C(5) is *cis* in **18**, but *trans* in **19**.

Fig. 1.

Since the results of the reactions under various conditions did not change, we tried to isolate a product from the yellow oil by varying the purification methods. Column chromatography on silica gel (acidic) or Alox (basic) did not lead to satisfying results; therefore, 1% Et<sub>3</sub>N was added to the eluent of the chromatography on silica gel. This procedure showed considerable advantage over all methods previously used and the best results were obtained with 3% Et<sub>3</sub>N. By using the same reaction conditions as described above and the new conditions for the chromatographic workup, the reactions of **14** with phenyldiazomethan (**15b**), diazomethane (**15d**), and (4-methoxyphenyl)diazomethan (**15e**) gave the expected 1,3-oxathiols **20a**, **21**, and

**20b** in yields of 42, 40, and 60%, respectively (*Scheme 4*). In addition to the main product, namely the 1,3-oxathiols, the corresponding alkenes, which result from a 1,3-dipolar electrocyclization of the thiocarbonyl ylide, followed by a desulphurization, were observed as by-products, and not the *Schönberg* products. These by-products were themselves reactive and led to further by-products, which were not isolated or characterized.

*Scheme 4*

The structure of **20b** was established by X-ray crystallography (*Fig. 2*). The five-membered ring has an envelope conformation with C(5) as the envelope flap. The planes of the Ph groups at C(2) and C(3) are twisted out of the plane defined by C(6), C(2), C(3), and C(12) by 57.6(2) and 33.1(2)°, respectively.

*Fig. 2.*

The results described above show that the synthesis of 1,3-oxathiols *via* 1,5-dipolar electrocyclization by starting from thioketones with a conjugated keto group, is achievable with moderate to good yields. Under the chosen conditions, the 1,3-dipolar electrocyclization is a side reaction. Comparing the yields from the different experiments shows that the substituents of the diazo-component have a significant influence on the yields of the desired 1,3-oxathiols. The highest yield (81%) was observed in the already known reaction of **14** with **15a**, which lead to 1,3-oxathiol **13** [11] (*Scheme 3*).

The reaction of diazocyclohexane (**15f**) with **14** in CH<sub>2</sub>Cl<sub>2</sub> at room temperature gave the sulphide **22** in 40% yield (*Scheme 4*). The structure of **22** was again established by X-ray crystallography (*Fig. 3*). The cyclohexane ring has two equally occupied disordered orientations which differ by a rotation of approximately 180° about the S-

C(15) bond. The formation of **22** is easily rationalized *via* the intermediate cycloadduct **23** and the thiocarbonyl ylide **24**, which does not undergo the 1,5-dipolar electrocyclization, but a [1,4]-H shift to give 2-[(cyclohex-1-enyl)sulfanyl]-1,2-diphenylethanone (**22**). Similar [1,4]-H shifts in thiocarbonyl ylides are known [5][6].

*Scheme 5*

*Fig. 3.*

The synthesis of the fused 1,3-thioxole **25** was achieved by starting from 2-[(2-oxocyclohexyl)sulfanyl]isoindole-1,3-dione (**26**) and generating the intermediate 2-thioxocyclohexanone (**27**) by DBU-catalyzed elimination of phthalimide [13][14] (*Scheme 6*). In the presence of excess diphenyldiazomethane (**15a**), **27** underwent a cycloaddition to yield **28**, which eliminated N<sub>2</sub> spontaneously to give the thiocarbonyl ylide **29**. The subsequent reaction followed the expected pathway *via* 1,5-dipolar cyclization. The same 1,3-oxathiole (**25**) has been synthesized by *Kelmendi et al.* [9]. In this case, the starting material was 2-diazocyclohexanone (**30**), which reacted with thiobenzophenone (**31**) to give the same intermediate **28**. Because of the special reaction conditions, only the reaction with diphenyldiazomethane (**15a**) was successful.

*Scheme 6*

The structure of **25** has been determined by X-ray crystallography (*Fig. 4*). The five-membered heterocycle has an envelope conformation with C(3) as the envelope flap, while the cyclohexene ring has a half-chair conformation twisted on C(7)-C(8).



2.2. *Reactions with  $\alpha$ -Thioxothioamides.* After these encouraging results with  $\alpha$ -thioxoketones, we tried to find other systems, which would react analogously.  $\alpha$ -Thioxothioamides of type **32** are easily available and possess an unsaturated system, the thioamide group, in conjugation with the thiocarbonyl group. The reactions of **32** with diazocompounds showed that thiocarbonyl ylides are formed, which undergo a 1,5-dipolar electrocyclization to yield 1,3-dithiols (**33-35**) (*Scheme 7*). In all cases, the yields of the heterocyclic product were lower than with the thioxocarbonyl compound **14**. In the reactions of **32** with **15b** and **15e**, respectively, the 1,3-dipolar electrocyclization of the intermediate thiocarbonyl ylide is a more significant side reaction than in the case of **14** and yields the corresponding  $\alpha,\beta$ -unsaturated thioamides **36** and **37** after desulfurization<sup>3</sup>). The only reaction in which no side product was formed was that between diphenyldiazomethane (**15a**) and **32**. As in the case of  $\alpha$ -thioxoketone **14**, the reaction of **32** with diazocyclohexane (**15f**) led to the thioenole **38** exclusively, which results from a [1,4]-H shift of the corresponding intermediate thiocarbonyl ylide. The reaction of **32** with diazomethane (**15d**) was carried out under the same conditions as those used in the case of **14**, but only decomposition was observed (TLC), and no reasonable product of a related reaction could be isolated.

*Scheme 7*

The structures of the 1,3-dithiole **33** and  $\alpha$ -sulfanylthioamide **38** have been established by X-ray crystallography (*Fig. 5*).

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<sup>3</sup>) These side products could not be obtained in pure form, but only as mixtures of (*E/Z*)-isomers.

Fig. 5.

**3. Conclusions.** We have investigated several reactions of diazo compounds with thioketones, which contain a keto or a thioamide group in the  $\alpha$ -position. The reactions proceeded *via* thiocarbonyl ylides as intermediates, which, in most cases underwent a 1,5-dipolar electrocyclization to give the corresponding five-membered ring containing the former thiocarbonyl S-atom, *i.e.*, 1,3-oxathioles and 1,3-dithioles, respectively. In some cases, a 1,3-dipolar electrocyclization of the thiocarbonyl ylide occurred to give the corresponding thiiranes, which spontaneously desulfurized to yield the corresponding alkenes. Since 1,3-oxathioles with an H-atom in the ring are generally unstable under acidic conditions, they decomposed during chromatography on acidic or wet silica gel, and in these cases the *Schönberg* products **17-19** could be isolated, though in relatively low yields (10-25%).

The diazo compound used also seems to be decisive for the reaction pathway. When the diazo compound bears at least one H-atom in the  $\beta$ -position to the diazo group, *e.g.* diazocyclohexane (**15f**), no products of the 1,5- nor of the 1,3-dipolar electrocyclization could be isolated from the reaction with **14** or **32**. The only products isolated in these cases are products resulting from a [1,4]-H shift in the intermediate thiocarbonyl ylide. The behaviour of the  $\alpha$ -thioxothioamide **32** under the chosen conditions is very much like that of  $\alpha$ -thioxoketones. However, the competition of the 1,3-dipolar electrocyclization of the thiocarbonyl ylide, which produces the corresponding alkenes, is more pronounced.

We thank the analytical units of our institute for spectra and analyses, and the *Swiss National Science Foundation* and *F. Hoffmann-La Roche AG*, Basel, for financial support.

## Experimental Part

1. *General*. Solvents were purified prior to use by standard procedures. TLC: Glass plates covered with silica gel 60 F<sub>254</sub> (*Merck*); visualization by UV light or by spraying with 'mostain' soln. (Ce(SO<sub>4</sub>)<sub>2</sub> (0.8 g), 10% H<sub>2</sub>SO<sub>4</sub> (800 ml)) and heating (blue spots). Column chromatography (CC): silica gel 60 (*Merck*), 0.040 ± 0.063 mm. Medium-pressure liquid chromatography (MPLC): *Labomat VS-200* of *Labomatic* with a *HPP-VPC*-column of *Kron-Lab* (length: 540 mm, inside Ø: 40mm, max. pressure: 40 bar) was used. M.p. (not corrected): *Mettler FP 5/52*. IR Spectra: *Perkin-Elmer 1600 Series FT-IR* spectrometer; in cm<sup>-1</sup>, characterization of the band intensities (transmission): 0 - 20% *vs*, 20 - 40% *s*, 40 - 60% *m*, 60 - 80% *w*. NMR Spectra: *Bruker ARX-300* (300 and 75.5 MHz, resp.); chemical shifts  $\delta$  (in ppm) relative to CDCl<sub>3</sub> (7.27 resp. 77.0 ppm), coupling constants *J* in Hz; for assignments of <sup>1</sup>H-NMR signals, COSY, TOCSY and NOESY 2D- or 1D-NMR methods were applied; for assignments of <sup>13</sup>C-NMR signals, HMBC and HSQC 2D-NMR methods were employed. If not stated otherwise, the spectra were recorded in CDCl<sub>3</sub>. MS: *Varian SSQ 700*; ionization by EI (70 eV) or CI (NH<sub>3</sub>); in *m/z*, rel. intensities (%).

2. *Starting Materials*. All thiocarbonyl derivatives or precursors and the diazo compounds were prepared following known protocols: diphenyldiazomethane (**15a**) [11], phenyldiazomethane (**15b**) [15], diazomethane (**15d**) [16], diazocyclohexane (**15f**) [17], 1,2-diphenyl-2-thioxoethanone (**14**) [11], *N,N*-dimethyl-2-phenyl-2-

thioxothioacetamide (**32**) [18], 2-[(2-oxocyclohexyl)sulfanyl]isoindole-1,3-dione (**26**) [13] [14]. All other reagents are commercially available.

3. *Yields*. Almost all of the diazo compounds are only stable in solution and were often used in excess. As most of the thiocarbonyl compounds were also only stable in solution, or they were synthesized *in situ*, the corresponding yields were approximated. The reported yields in these cases are based on experience [11] or on the volume of N<sub>2</sub> evolved. When this was not possible, *i.e.* in cases of reactions lasting two or more days, yields were calculated over two or three reaction steps.

4. *General Procedure A (GP A)*: To a soln. of thiocarbonyl compound (2-7 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (30-100 ml), the diazo compound (1-7 mmol) in toluene or benzene (30-130 ml) was added by means of a dropping funnel. After total conversion of the thiocarbonyl compound, monitored either by TLC, color change or evolution of N<sub>2</sub><sup>4</sup>), the solvent was evaporated and the mixture was analyzed and purified by chromatography using silica gel, which had been treated with 3% Et<sub>3</sub>N. Furthermore, the solvent was doped with 1% of Et<sub>3</sub>N.

*General Procedure B (GP B)*: The same procedure as in *GP A* was followed, but the mixture was purified by chromatography without using Et<sub>3</sub>N.

*General Procedure C (GP C)*: To a suspension of isoindole-1,3-dione **26** (2-5 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (15-40 ml) at -10°, **15a** was added as a purple soln. in benzene (10-25 ml, 3-7 mmol). A catalytic amount of DBU was added and the evolution of N<sub>2</sub> was measured volumetrically. After stirring for a few min, the solvent was removed and the mixture was analysed and purified by chromatography.

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<sup>4</sup>) The evolution of N<sub>2</sub> was determined volumetrically using a gas burette attached to the reaction vessel.

5. *Reactions of 1,2-Diphenyl-2-thioxoethanone (14) with Diazoalkanes.*

*2,4-trans-4,5-trans-(4-Benzoyl-2,4,5-triphenyl-1,3-dithiolane-2-yl)phenylmethanone (17).* According to *GP B*, **14** (3.9 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (60 ml) and **15b** (*ca.* 3.9 mmol) in toluene (150 ml) were used. The crude product was purified by CC (hexane/AcOEt 20:1) and recrystallized from hexane/AcOEt: 371 mg (20%) of **17**. Colorless crystals. M.p. 232-233°. IR (KBr): 3058<sub>w</sub>, 3028<sub>w</sub>, 2928<sub>w</sub>, 1679<sub>vs</sub>, 1595<sub>s</sub>, 1479<sub>m</sub>, 1489<sub>m</sub>, 1445<sub>s</sub>, 1395<sub>w</sub>, 1308<sub>w</sub>, 1228<sub>vs</sub>, 1184<sub>s</sub>, 1156<sub>w</sub>, 1080<sub>w</sub>, 1036<sub>w</sub>, 1018<sub>m</sub>, 1001<sub>w</sub>, 971<sub>w</sub>, 934<sub>w</sub>, 878<sub>w</sub>, 861<sub>w</sub>, 839<sub>w</sub>, 826<sub>w</sub>, 807<sub>w</sub>, 785<sub>w</sub>, 771<sub>w</sub>, 753<sub>m</sub>, 740<sub>s</sub>, 696<sub>vs</sub>, 685<sub>s</sub>, 658<sub>s</sub>, 650<sub>s</sub>. <sup>1</sup>H-NMR: 7.78-7.72 (*m*, 4 arom. H); 7.64-7.61 (*m*, 2 arom. H); 7.49-6.89 (*m*, 19 arom. H); 5.85 (*s*, H-C(5)). <sup>13</sup>C-NMR: 193.5, 191.5 (2<sub>s</sub>, 2 CO); 141.1, 135.8, 135.6, 134.1, 133.6 (5<sub>s</sub>, 5 arom. C); 133.3, 132.6, 130.7, 130.5, 130.1, 129.0, 128.4, 128.2, 128.0, 127.9, 127.8, 127.4, 126.6 (13<sub>d</sub>, 25 arom. CH); 79.5 (*s*, C(4)); 60.1 (*d*, C(5))<sup>5</sup>. CI-MS: 560 (100, [*M* + NH<sub>4</sub>]<sup>+</sup>), 543 (54, [*M* + 1]<sup>+</sup>), 317 (67, [*M* - PhCOCSPh]<sup>+</sup>), 285 (41), 244 (28), 214 (19). Anal. calc. for C<sub>35</sub>H<sub>26</sub>O<sub>2</sub>S<sub>2</sub> (542.72): C 77.46, H 4.83, S 11.82; found: C 77.51, H 4.91, S 11.80.

Crystals suitable for an X-ray crystal-structure determination were grown from CH<sub>2</sub>Cl<sub>2</sub>/hexane by slow evaporation of the solvent.

*Ethyl 2,4-cis-4,5-cis-4,5-Dibenzoyl-4,5-diphenyl-1,3-dithiolane-2-carboxylate (18).*

According to *GP B*, **14** (3.9 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (60 ml) and ethyl diazoacetate (1.02 g, 8.9 mmol; **15c**) in Et<sub>2</sub>O (20 ml) were used. The crude product was purified by CC (hexane/AcOEt 10:1) and the product recrystallized from hexane/AcOEt: 458 mg,

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<sup>5</sup>) The signal for C(2) could not be detected.

(25%) of **18**. Colorless crystals. M.p. 195-197°. IR (KBr): 3058<sub>w</sub>, 3031<sub>w</sub>, 2984<sub>w</sub>, 2898<sub>w</sub>, 1710<sub>vs</sub>, 1697<sub>vs</sub>, 1673<sub>vs</sub>, 1595<sub>m</sub>, 1578<sub>m</sub>, 1490<sub>m</sub>, 1464<sub>w</sub>, 1445<sub>vs</sub>, 1395<sub>w</sub>, 1368<sub>w</sub>, 1221<sub>vs</sub>, 1182<sub>vs</sub>, 1160<sub>m</sub>, 1086<sub>w</sub>, 1022<sub>vs</sub>, 1002<sub>w</sub>, 971<sub>w</sub>, 959<sub>w</sub>, 933<sub>w</sub>, 900<sub>w</sub>, 872<sub>w</sub>, 850<sub>w</sub>, 806<sub>w</sub>, 790<sub>w</sub>, 766<sub>s</sub>, 715<sub>vs</sub>, 698<sub>vs</sub>, 660<sub>m</sub>, 642<sub>vs</sub>. <sup>1</sup>H-NMR ((D<sub>6</sub>)-DMSO): 7.57-6.61 (*m*, 20 arom. H); 5.89 (*s*, H-C(2)); 3.78 (*qd*-like, CH<sub>2</sub>); 0.70 (*t*, *J* = 7.1, Me). <sup>13</sup>C-NMR ((D<sub>6</sub>)-DMSO): 195.1, 191.8 (2<sub>s</sub>, 2 CO); 167.9 (*s*, C(O)O); 139.4, 136.6, 135.7, 133.2 (4<sub>s</sub>, 4 arom. C); 132.3, 131.4, 130.2, 129.2, 128.2, 127.9, 127.4, 127.2, 126.8 (9<sub>d</sub>, 20 arom. H); 80.8, 79.4 (2<sub>s</sub>, C(4), C(5)); 61.6 (*t*, CH<sub>2</sub>); 47.6 (*d*, C(2)); 13.0 (*q*, Me)<sup>6</sup>. CI-MS: 556 (7, [*M* + NH<sub>4</sub>]<sup>+</sup>), 539 (9, [*M* + 1]<sup>+</sup>), 390 (31), 389 (100). Anal. calc. for C<sub>32</sub>H<sub>26</sub>O<sub>4</sub>S<sub>2</sub> (538.69): C 71.35, H 4.87, S 11.91; found: C 71.37, H 4.68, S 11.62.

Crystals suitable for an X-ray crystal-structure determination were grown from CH<sub>2</sub>Cl<sub>2</sub>/AcOEt by slow evaporation of the solvent.

*trans*-(5-Benzoyl-4,5-diphenyl-1,3-dithiolane-4-yl)phenylmethanone (**19**). According to *GP B* **14** (3.9 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (60 ml) and **15d** (*ca.* 4-6 mmol) in Et<sub>2</sub>O (8 ml) were used. After 10 min stirring, a small amount of AcOH was added dropwise until the N<sub>2</sub>-evolution ceased. The crude product was purified by CC (hexane/AcOEt 10:1): 302 mg (15%) of **19**. Colorless crystals. M.p. 189° (decomp.). IR (KBr): 3087<sub>w</sub>, 3061<sub>m</sub>, 3030<sub>w</sub>, 2985<sub>w</sub>, 2929<sub>w</sub>, 1681<sub>vs</sub>, 1594<sub>s</sub>, 1578<sub>s</sub>, 1493<sub>s</sub>, 1444<sub>vs</sub>, 1414<sub>m</sub>, 1317<sub>w</sub>, 1302<sub>w</sub>, 1216<sub>vs</sub>, 1197<sub>vs</sub>, 1182<sub>vs</sub>, 1100<sub>m</sub>, 1085<sub>m</sub>, 1035<sub>m</sub>, 1010<sub>vs</sub>, 973<sub>w</sub>, 937<sub>w</sub>, 871<sub>w</sub>, 842<sub>w</sub>, 786<sub>w</sub>, 769<sub>s</sub>, 753<sub>w</sub>, 742<sub>w</sub>, 700<sub>vs</sub>, 638<sub>w</sub>, 611<sub>vs</sub>. <sup>1</sup>H-NMR:

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<sup>6</sup>) Because of the doubling of some signals, the compound is either a mixture of isomers or conformers.

7.39-7.35 (*m*, 8 arom. H); 7.25-7.15 (*m*, 8 arom. H); 7.08-7.03 (*m*, 4 arom. H); 3.96 (*s*, CH<sub>2</sub>). <sup>13</sup>C-NMR: 190.0 (*s*, 2 CO); 136.2, 133.3 (2*s*, 4 arom. C); 132.9, 131.0, 130.1, 128.3, 127.3, 126.9 (6*d*, 20 arom. CH); 78.5 (*s*, C(4), C(5)); 32.3 (*t*, CH<sub>2</sub>). EI- and CI-MS: no measurement possible. Anal. calc. for C<sub>29</sub>H<sub>22</sub>O<sub>2</sub>S<sub>2</sub> (466.63): C 74.65, H 4.75, S 13.74; found: C 74.90, H 4.61, S 13.45.

Crystals suitable for an X-ray crystal-structure determination were grown from AcOEt by slow evaporation of the solvent.

*4,5-Diphenyl-1,3-oxathiole (21)*. According to *GP A*, **14** (*ca.* 4 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (83 ml) and **15d** (*ca.* 5 mmol) in Et<sub>2</sub>O (*ca.* 50 ml) were used. The crude product was purified by CC (hexane/AcOEt 4:1 + 3% Et<sub>3</sub>N) and recrystallized from hexane/Et<sub>2</sub>O: 368 mg (*ca.* 40%) of **21**. Yellowish crystals. M.p. 41-43°. IR (Golden Gate, ATR): 3057*w*, 3032*w*, 2915*w*, 2856*w*, 1691*w*, 1616*m*, 1593*m*, 1571*m*, 1494*m*, 1443*m*, 1329*m*, 1313*w*, 1297*w*, 1208*m*, 1072*w*, 1058*s*, 1028*m*, 1000*m*, 988*m*, 942*s*, 924*m*, 847*m*, 771*m*, 755*vs*, 742*s*, 693*vs*, 675*s*. <sup>1</sup>H-NMR: 7.36-7.18 (*m*, 10 arom. H); 5.69 (*s*, H<sub>2</sub>C(2)). <sup>13</sup>C-NMR: 143.9 (*s*, C(5)); 132.4, 130.4 (2*s*, 2 arom. C); 129.0, 128.5, 128.2, 128.0, 127.7, 127.4 (6*d*, 10 arom. CH); 111.4 (*s*, C(4)); 72.7 (*t*, H<sub>2</sub>C(2)). CI-MS (NH<sub>3</sub>): 242 (17), 241 (100, [*M* + 1]<sup>+</sup>).

*2,4,5-Triphenyl-1,3-oxathiole (20a)*. According to *GP A*, **14** (*ca.* 2.4 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (30 ml) and **15b** (*ca.* 3 mmol) in toluene (100 ml) were used. The crude product was purified by CC (hexane/AcOEt 5:1 + 3% Et<sub>3</sub>N) and recrystallized from hexane/CH<sub>2</sub>Cl<sub>2</sub>: 317 mg (*ca.* 45%) of **20a**. Yellowish crystals. M.p. 74-75°. IR (Golden Gate, ATR): 3058*w*, 3034*w*, 2887*w*, 2868*w*, 1620*w*, 1598*w*, 1573*w*, 1494*w*,

1453w, 1444w, 1318w, 1248m, 1215w, 1056m, 1024w, 990m, 954m, 916w, 877w, 827w, 780w, 752s, 715m, 692s, 684s. <sup>1</sup>H-NMR: 7.66-7.21 (*d*-like, 2 arom. H); 7.44-7.17 (*m*, 13 arom. H); 7.04 (*s*, HC(2)). <sup>13</sup>C-NMR: 142.6 (*s*, C(5)); 139.6, 132.5, 130.6 (3*s*, 3 arom. C); 129.2, 129.1, 128.7, 128.3, 128.2, 127.8, 127.6, 126.4 (8*d*, 15 arom. CH); 111.3 (*s*, C(4)); 87.3 (*d*, HC(2)). CI-MS (NH<sub>3</sub>): 318 (22), 317 (100, [*M* + 1]<sup>+</sup>). Anal. calc. for C<sub>21</sub>H<sub>16</sub>OS: C 79.71, H 5.10, S 10.13; found: C 79.62, H 4.95, S 10.17.

*2-(4-Methoxyphenyl)-4,5-diphenyl-1,3-oxathiole (20b)*. According to *GP A*, **14** (*ca.* 2 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (30 ml) and **15e** (*ca.* 3 mmol) in benzene (20 ml) were used. The crude product was purified by CC (hexane/AcOEt 30:1 + 1% Et<sub>3</sub>N) and recrystallized from hexane/CH<sub>2</sub>Cl<sub>2</sub>: 410 mg (40-55%) of **20b**. Yellowish crystals. M.p. 104-108°. IR (Golden Gate, ATR): 3056w, 3007w, 2956w, 2928w, 2906w, 2869w, 2834w, 1686w, 1625w, 1609m, 1585w, 1511s, 1494m, 1464w, 1443m, 1356w, 1317w, 1305m, 1289w, 1243vs, 1218m, 1171s, 1107w, 1082w, 1056s, 1026s, 984m, 956m, 915w, 881w, 833s, 777m, 763m, 754s, 697s, 683s. <sup>1</sup>H-NMR: 7.63-7.58 (*d*-like, 2 arom. H); 7.39-7.18 (*m*, 10 arom. H); 7.01 (*s*, HC(2)); 6.96-6.91 (*d*-like, 2 arom. H); 3.82 (*s*, MeO). <sup>13</sup>C-NMR: 160.4 (*s*, 1 arom. C); 143.0 (*s*, C(5)); 132.6, 131.4, 130.7 (3*s*, 3 arom. C); 129.1, 128.6, 128.2, 128.1, 127.7, 127.6 (6*d*, 12 arom. CH); 114.0 (*d*, 2 arom. CH); 111.8 (*s*, C(4)); 87.4 (*d*, C(2)); 55.4 (*q*, MeO). CI-MS (NH<sub>3</sub>): 348 (24), 347 (100, [*M* + 1]<sup>+</sup>), 315 (39, [*M* - MeO]<sup>+</sup>). ESI-MS: 369 (100, [*M* + Na]<sup>+</sup>).

Crystals suitable for an X-ray crystal-structure determination were grown from hexane/AcOEt by slow evaporation of the solvent.



2-[(Cyclohexen-1-yl)sulfanyl]-1,2-diphenylethanone (**22**). According to *GP B*, a soln. of **15f** (*ca.* 7 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (40 ml) was added dropwise to a soln. of **14** (*ca.* 6.4 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (100 ml). Purification of the crude product by MPLC (hexan/AcOEt 20:1) afforded 790 mg (40%) of **22**. Yellowish crystals. M.p. 61-63°. IR (KBr): 3062<sub>w</sub>, 3027<sub>w</sub>, 2936<sub>vs</sub>, 2909<sub>s</sub>, 2859<sub>s</sub>, 2834<sub>m</sub>, 1672<sub>vs</sub>, 1596<sub>s</sub>, 1580<sub>s</sub>, 1493<sub>m</sub>, 1451<sub>vs</sub>, 1433<sub>m</sub>, 1342<sub>m</sub>, 1322<sub>m</sub>, 1307<sub>m</sub>, 1296<sub>m</sub>, 1274<sub>s</sub>, 1212<sub>m</sub>, 1191<sub>s</sub>, 1169<sub>s</sub>, 1136<sub>m</sub>, 1075<sub>m</sub>, 1054<sub>w</sub>, 1007<sub>s</sub>, 999<sub>s</sub>, 929<sub>w</sub>, 914<sub>m</sub>, 868<sub>w</sub>, 844<sub>w</sub>, 831<sub>w</sub>, 797<sub>w</sub>, 782<sub>w</sub>, 758<sub>s</sub>, 723<sub>s</sub>, 694<sub>vs</sub>, 681<sub>s</sub>, 640<sub>s</sub>. <sup>1</sup>H-NMR ((D<sub>6</sub>)-DMSO): 8.09-8.06 (*m*, 2 arom.H); 7.64-7.59 (*m*, 1 arom. H); 7.52-7.47 (*m*, 4 arom. H); 7.35-7.24 (*m*, 3 arom. H); 6.22 (*s*, H-C(2)); 5.70-5.68 (*m*, =CH)<sup>7</sup>; 1.94-1.40 (*m*, 4 CH<sub>2</sub>). <sup>13</sup>C-NMR ((D<sub>6</sub>)-DMSO): 195.0 (*s*, CO); 136.8, 135.3 (2*s*, 2 arom. C); 130.6 (*s*, =C-S); 133.5 (*d*, C(2)); 129.3, 128.7, 128.4, 127.6 (4*d*, 10 arom. CH); 54.1 (*d*, =CH); 30.1, 25.9, 22.8, 21.1 (4*t*, 4 CH<sub>2</sub>). CI-MS: 310 (23), 309 (100, [*M* + 1]<sup>+</sup>), 214 (32). Anal. calc. for C<sub>20</sub>H<sub>20</sub>OS (308.44): C 77.88, H 6.54, S 10.40; found: C 77.69, H 6.37, S 10.10.

Crystals suitable for an X-ray crystal-structure determination were grown from hexane/AcOEt by slow evaporation of the solvent.

#### 6. Reaction of 2-Thioxocyclohexanone (**37**) with Diphenyldiazomethane (**15a**).

2,2-Diphenyl-4,5,6,7-tetrahydrobenzo-1,3-oxathiole (**25**). According to *GP C*, a suspension of 2-[(2-oxocyclohexyl)sulfanyl]isoindole-1,3-dione (**26**; 1.0 g, 3.6 mmol) [13][14] was treated with a catalytic amount of DBU and an excess of **15a** in Et<sub>2</sub>O. CC (hexane/AcOEt 15:1) yielded 702 mg (51%) of **25**. Pale-bluish crystals. M.p. 107-109°. IR (KBr): 3080<sub>w</sub>, 3059<sub>w</sub>, 3019<sub>w</sub>, 3001<sub>w</sub>, 2950<sub>s</sub>, 2917<sub>s</sub>, 2884<sub>m</sub>,

<sup>7</sup>) When the spectrum was recorded in CDCl<sub>3</sub>, the signals of HC(2) and =CH overlap.

2855 $m$ , 2841 $s$ , 1682 $s$ , 1598 $w$ , 1585 $w$ , 1488 $s$ , 1445 $vs$ , 1388 $w$ , 1353 $w$ , 1340 $m$ , 1313 $w$ , 1289 $w$ , 1261 $w$ , 1225 $m$ , 1206 $s$ , 1176 $vs$ , 1145 $vs$ , 1133 $s$ , 1109 $w$ , 1071 $m$ , 1028 $s$ , 997 $m$ , 986 $vs$ , 958 $s$ , 933 $w$ , 916 $m$ , 900 $m$ , 882 $s$ , 857 $w$ , 836 $w$ , 819 $w$ , 763 $vs$ , 754 $vs$ , 696 $vs$ .  $^1\text{H}$ -NMR : 7.54-7.50 ( $m$ , 4 arom. H); 7.34-7.23 ( $m$ , 6 arom. H); 2.29-2.24 ( $m$ , 2 H); 2.17-2.12 ( $m$ , 2 H); 1.73-1.65 ( $m$ , 4 H).  $^{13}\text{C}$ -NMR: 144.7 ( $s$ , 2 arom. C); 143.1 ( $s$ , C(7a)); 128.0, 127.9, 126.4 (3 $d$ , 10 arom. CH); 104.5, 100.7 (2 $s$ , C(2), C(3a)); 24.2, 23.5, 23.0, 22.4 (4 $t$ , 4  $\text{CH}_2$ ). EI-MS: 294 (26,  $M^+$ ), 266 (11), 262 (23), 261 (100), 237 (28), 223 (13), 187 (15), 167 (18), 166 (10), 165 (49), 105 (21,  $[\text{PhCO}]^+$ ), 77 (14,  $\text{Ph}^+$ ). Anal. calc. for  $\text{C}_{19}\text{H}_{18}\text{OS}$  (294.42): C 77.51, H 6.16; found: C 77.49, H 6.08.

Crystals suitable for an X-ray crystal-structure determination were grown from hexane by slow evaporation of the solvent.

#### 7. Reactions of *N,N*-Dimethyl-2-phenyl-2-thioxothioacetamide (**32**) with Diazoalkanes.

*N,N*-Dimethyl-*N*-(2,2,5-triphenyl-1,3-dithiol-4-yl)amine (**33**). According to GP A, a soln. of **32** (200 mg, 1.1 mmol) in  $\text{CH}_2\text{Cl}_2$  (20 ml) and **15a** (ca. 1.5 mmol) in benzene (15 ml) were used. The crude product was purified by CC (hexane/AcOEt 10:1 to 4:1): 170 mg (ca. 43%) of **33**. Yellowish crystals. M.p. 122-125°. IR: 3053 $w$ , 3013  $m$ , 2986  $m$ , 2950  $m$ , 2923  $m$ , 2897  $m$ , 2862  $m$ , 2834  $m$ , 2792  $m$ , 1659  $w$ , 1590  $m$ , 1570  $s$ , 1553  $vs$ , 1483  $vs$ , 1452  $s$ , 1440  $vs$ , 1406  $m$ , 1311  $s$ , 1210  $m$ , 1071  $s$ , 1045  $s$ , 1033  $s$ , 998  $m$ , 961  $m$ , 902  $m$ , 861  $s$ , 833  $m$ , 800  $w$ , 756  $vs$ , 737  $vs$ , 698  $vs$ , 690  $vs$ , 658  $s$ , 629  $m$ , 618  $m$ , 608  $m$ .  $^1\text{H}$ -NMR: 7.62-7.54 ( $d$ -like, 4 arom. CH); 7.43-7.37 ( $d$ -like, 2 arom. CH); 7.25-7.05 ( $m$ , 9 arom. CH); 2.42 ( $s$ ,  $\text{Me}_2\text{N}$ ).  $^{13}\text{C}$ -NMR: 143.7 ( $s$ , 2 arom. C); 142.7 ( $s$ , arom. C); 134.5 ( $s$ , C(4)); 129.2, 128.3, 128.0, 127.9, 127.8,

127.4, 126.7 (7d, 15 arom. C); 117.6 (s, C(5)); 70.5 (s, C(2)); 44.2 (q, Me<sub>2</sub>N). CI-MS (NH<sub>3</sub>): 378 (12), 377 (28), 376 (100, [M + 1]<sup>+</sup>), 344 (24, [M-S + 1]<sup>+</sup>), 199 (17), 180 (15).

Crystals suitable for an X-ray crystal-structure determination were grown from hexane/CH<sub>2</sub>Cl<sub>2</sub> by slow evaporation of the solvent.

N-(2,5-Diphenyl-1,3-dithiol-4-yl)-N,N-dimethylamine (**34**). According to GP A, a suspension of **32** (250 mg, 1.2 mmol) in toluene (20 ml) and **15b** (ca. 15 mmol) in toluene (100 ml) were used. The mixture was separated by CC (hexane/AcOEt 10:1 + 1% Et<sub>3</sub>N): 90 mg (ca. 25%) of **34** and 80 mg (ca. 25%) of a mixture of (*E*)- and (*Z*)-N,N-Dimethyl-2,3-diphenylthioacrylamide (**36**). Data of **34**: Yellowish oil. IR (KBr): 3059m, 3026m, 2932m, 2863m, 2788w, 1679s, 1647vs (enamin), 1597s, 1580s, 1554m, 1514s, 1493vs, 1451vs, 1392vs, 1333w, 1273s, 1206m, 1176m, 1142s, 1073s, 1030m, 1001w, 993w, 963w, 939w, 905w, 886w, 860w, 837w, 808w, 782w, 755s, 726s, 697vs. <sup>1</sup>H-NMR: 7.62-7.51 (m, 4 arom. H); 7.36-7.18 (m, 6 arom. H); 5.78 (s, HC(2)); 2.59 (s, Me<sub>2</sub>N). <sup>13</sup>C-NMR: 141.4 (s, C(4)); 141.1, 134.1 (2s, 2 arom. C); 128.6, 128.2, 128.0, 126.9, 126.7 (5d, 10 arom. CH); 115.1 (s, C(5)); 50.0 (d, C(2)); 44.2 (q, Me<sub>2</sub>N). CI-MS (NH<sub>3</sub>): 301 (21), 300 (100, [M + 1]<sup>+</sup>).

Data of **36**: IR (KBr): 3078m, 3054m, 3022m, 2929s, 2857m, 1598m, 1574w, 1513vs, 1494vs, 1446vs, 1391vs, 1318w, 1269vs (CSNMe<sub>2</sub>), 1203w, 1181m, 1146vs, 1116vs, 1076s, 1049m, 1030m, 1000w, 949m, 922m, 886m, 870w, 796w, 765vs, 714vs, 695vs. <sup>1</sup>H-NMR: 7.57-7.06 (m, 10 arom. H); 6.73, 6.69 (2s (1:3.5), =CH); 3.56, 3.49, 3.28, 3.12 (4s (1:3:3:1), Me<sub>2</sub>N). <sup>13</sup>C-NMR (only the signals of the main isomer are given): 201.7 (s, CS); 143.4 (s, C(2)); 135.8, 135.5 (2s, 2 arom. C); 129.3,

128.7, 128.6, 128.5, 128.1, 127.8, 127.4 (*7d*, 10 arom. CH, =CH); 43.1, 42.9 (*2q*, Me<sub>2</sub>N). CI-MS (NH<sub>3</sub>): 269 (19), (268, 100 [*M* + 1]<sup>+</sup>).

*N*-[2-(4-Methoxyphenyl)-5-phenyl-1,3-dithiol-4-yl]-*N,N*-dimethylamine (35).

According to *GP A*, a suspension of **32** (280 mg, 1.34 mmol) in toluene (20 ml) and **15e** (*ca.* 2 mmol) in benzene (20 ml) were used. The mixture was separated by CC (hexane/AcOEt 10:1 + 1% Et<sub>3</sub>N): 80 mg (*ca.* 20%) of **35**, and 52 mg (*ca.* 13%) of (*E/Z*)-3-(4-Methoxyphenyl)-*N,N*-dimethyl-2-phenylthioacrylamide (**37**). Data of **35**: Yellowish oil. IR (Golden Gate, ATR): 3058<sub>w</sub>, 3026<sub>w</sub>, 2931<sub>w</sub>, 2362<sub>w</sub>, 1678<sub>w</sub>, 1645<sub>m</sub>, 1596<sub>w</sub>, 1579<sub>w</sub>, 1551<sub>w</sub>, 1492<sub>w</sub>, 1449<sub>m</sub>, 1393<sub>w</sub>, 1314<sub>w</sub>, 1266<sub>w</sub>, 1244<sub>w</sub>, 1206<sub>w</sub>, 1175<sub>w</sub>, 1144<sub>w</sub>, 1103<sub>w</sub>, 1073<sub>w</sub>, 1028<sub>w</sub>, 993<sub>w</sub>, 904<sub>w</sub>, 846<sub>w</sub>, 755<sub>w</sub>, 725<sub>m</sub>, 694<sub>s</sub>. <sup>1</sup>H-NMR: 7.55-7.51 (*m*, 4 arom. H); 7.32-7.18 (*m*, 3 arom. H); 6.88-6.83 (*m*, 2 arom. H); 5.80 (*s*, HC(2)); 3.79 (*s*, MeO); 2.59 (*s*, Me<sub>2</sub>N). <sup>13</sup>C-NMR: 159.6 (*s*, arom. C); 141.4 (*s*, C(4)); 134.1, 133.0, 129.9 (3<sub>s</sub>, 3 arom. C); 128.2, 128.2, 128.0, 126.6 (4<sub>d</sub>, 7 arom. CH); 113.9 (*d*, 2 arom. CH); 55.2 (*q*, MeO); 49.9 (*d*, HC(2)); 44.2 (*q*, Me<sub>2</sub>N). CI-MS (NH<sub>3</sub>): 331 (21), 330 (100, [*M* + 1]<sup>+</sup>).

Data of **37**<sup>8</sup>): <sup>1</sup>H-NMR: 8.60 (*s*, =CH); 7.79-7.76 (*d*-like, arom. H); 7.54-7.51 (*d*-like, arom. H); 7.46-7.25 (*m*, arom. H), 7.03-6.81 (*m*, arom. H); 6.69-6.64 (*s*, =CH); 3.81, 3.74 (2<sub>s</sub> (1:4), MeO); 3.57, 3.48, 3.27, 3.13 (4<sub>s</sub> (1:3:3:1), Me<sub>2</sub>N). <sup>13</sup>C-NMR: 202.1 (*s*, CS); 159.0 (*s*, arom. C); 141.6, 136.2 (2<sub>s</sub>, 2 arom. C); 130.7, 129.3, 128.6, 127.9 (4<sub>d</sub>, 7 arom. CH); 113.4 (*d*, 2 arom. CH); 55.2 (*s*, MeO); 43.2, 43.0 (2<sub>q</sub>, Me<sub>2</sub>N). CI-MS (NH<sub>3</sub>): 299 (21), 298 (100, [*M* + 1]<sup>+</sup>), 269 (14, [*M*-Me<sub>2</sub>NH + NH<sub>3</sub>]<sup>+</sup>).

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<sup>8</sup>) Some signals of the NMR-spectra indicate the presence of (*E/Z*)-isomers of **37**. In the <sup>13</sup>C-NMR spectrum, only signals of the main isomer are given.

*2-[(Cyclohexen-1-yl)sulfanyl]-N,N-dimethyl-2-phenylethanethioamide* (**38**).

According to *GP A*, a soln. of **32** (313 mg, 1.5 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (25 ml) and **15f** (ca. 2 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (15 ml) were used. The crude product was purified by CC (hexane/AcOEt 10:1 to 4:1): 240 mg (ca. 55%) of **38**. Yellowish crystals. M.p. 110–111°. IR: 3079<sub>w</sub>, 3053<sub>w</sub>, 3024<sub>m</sub>, 3002<sub>w</sub>, 2940<sub>vs</sub>, 2918<sub>vs</sub>, 2851<sub>s</sub>, 2826<sub>s</sub>, 2657<sub>w</sub>, 1636<sub>w</sub>, 1600<sub>w</sub>, 1511<sub>vs</sub>, 1493<sub>vs</sub>, 1452<sub>s</sub>, 1435<sub>s</sub>, 1413<sub>s</sub>, 1385<sub>vs</sub>, 1339<sub>m</sub>, 1267<sub>vs</sub>, 1237<sub>s</sub>, 1182<sub>m</sub>, 1133<sub>vs</sub>, 1110<sub>vs</sub>, 1072<sub>m</sub>, 1051<sub>m</sub>, 1036<sub>m</sub>, 911<sub>w</sub>, 901<sub>w</sub>, 846<sub>w</sub>, 830<sub>w</sub>, 796<sub>m</sub>, 752<sub>m</sub>, 728<sub>vs</sub>, 698<sub>s</sub>, 640<sub>w</sub>. <sup>1</sup>H-NMR: 7.55–7.52 (*d*-like, 2 arom. H); 7.35–7.23 (*m*, 3 arom. H); 5.86–5.83 (*m*, =CH); 5.5.9 (*s*, HC(2)); 3.47, 3.22 (2*s*, Me<sub>2</sub>N) 2.22–2.00 (*m*, 4 H, cyclohexenyl); 1.69–1.49 (*m*, 4 H, cyclohexenyl). <sup>13</sup>C-NMR: 199.8 (*s*, C=S); 137.8 (*s*, arom. C); 132.0 (*d*, arom. C); 131.8 (*s*, =C-S); 128.3, 127.7, 127.6 (3*d*, 4 arom. C); 60.3 (*d*, C(2)); 45.3, 42.4 (*q*, Me<sub>2</sub>N); 30.8, 26.6, 23.3, 21.5 (4*t*, 4 CH<sub>2</sub>). EI-MS: 291 (9, *M*<sup>+</sup>), 259 (40, [*M*-S]<sup>+</sup>), 216 (20, [*M*-S-Me<sub>2</sub>N]<sup>+</sup>), 182 (22), 178 (52, [*M*-S-cyclohexenyl]<sup>+</sup>) 146 (100, [*M*-2S-cyclohexenyl]<sup>+</sup>), 131 (39), 116 (19).

Crystals suitable for an X-ray crystal-structure determination were grown from hexane/CH<sub>2</sub>Cl<sub>2</sub> by slow evaporation of the solvent.

8. *X-Ray Crystal-Structure Determination of 17, 18, 19, 20b, 22, 25, 33, and 38* (Tables 1 and 2 and Figs. 1–5)<sup>9</sup>). In the case of **17**, all measurements were made on a *Rigaku AFC5R* diffractometer using graphite-monochromated MoK<sub>α</sub> radiation ( $\lambda$

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<sup>9</sup>) CCDC-608137–608144 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the *Cambridge Crystallographic Data Center* via [http://www.ssd.c.cam.ac.uk/data\\_request/cif](http://www.ssd.c.cam.ac.uk/data_request/cif).

0.71073 Å) and a 12 kW rotating anode generator. In all other cases, all measurements were performed on a *Nonius KappaCCD* diffractometer [19] using graphite-monochromated MoK $\alpha$  radiation ( $\lambda$  0.71073 Å) and an *Oxford Cryosystems Cryostream* 700 cooler. The data collection and refinement parameters are given in *Tables 1* and *2*, and views of the molecules are shown in *Figs. 1-5*. For **17**, the intensities were corrected for *Lorentz* and polarization effects, but not for absorption. Equivalent reflections were merged. For all other structures, data reduction was performed with *HKL Denzo* and *Scalepack* [20]. The intensities were corrected for *Lorentz* and polarization effects, and with the exception of **18**, an absorption correction based on the multi-scan method [21] was applied. Equivalent reflections were merged, except for the *Friedel* pairs in **20b** and **33**. The structures were solved by direct methods using SHELXS97 [22] (**17**, **18**) and SIR92 [23] (**19**, **20b**, **22**, **25**, **33**, **38**), which revealed the positions of all non-H-atoms. In the case of **18**, the terminal Me group of the ethyl ester side chain is disordered and two equally occupied positions were refined for this group. The cyclohexene ring of **22** is also disordered and the two conformations differ by a rotation of approximately 180° about the S-C(15) bond. Two positions with equal site occupation factors were defined for each unsubstituted C-atom in the ring. However, some poor C-C bond lengths and elongated atomic displacement ellipsoids when these atoms were refined anisotropically suggest that the model does not fully describe the disorder and that the ring may adopt several conformations. The non-H-atoms were refined anisotropically in all structures, except for the disordered atoms of **22**, which were refined only isotropically. All of the H-atoms were placed in geometrically calculated positions and refined using a riding model where each H-atom was

assigned a fixed isotropic displacement parameter with a value equal to 1.2 U<sub>eq</sub> of its parent C-atom (1.5 U<sub>eq</sub> for the methyl groups in **20b**, **33** and **38**). The refinement of the structures **17**, **18**, **19**, **20b**, **22**, and **25** was carried out on  $F$  using full-matrix least-squares procedures, which minimized the function  $\sum w(|F_o| - |F_c|)^2$ . The refinement of **33** and **38** was carried out on  $F^2$  using full-matrix least-squares procedures, which minimized the function  $\sum w(F_o^2 - F_c^2)^2$ . A correction for secondary absorption was applied in the cases of **18** and **20b**. Compound **33** is achiral, but crystallized in a non-centrosymmetric space group. Refinement of the absolute structure parameter [24] yielded a value of 0.00(5), which confidently confirms that the refined coordinates represent the true absolute structure. The absolute structure parameter for **20b** refined to 0.35(15), which is insufficiently precise to be able to deduce any information about the absolute configuration of the molecule. The presence of an inversion twin cannot be excluded. According to the preparation of the material, it has to be racemic. Neutral atom scattering factors for non-H-atoms were taken from [25a], and the scattering factors for H-atoms were taken from [26]. Anomalous dispersion effects were included in  $F_c$  [27]; the values for  $f'$  and  $f''$  were those of [25b]. The values of the mass attenuation coefficients are those of [25c]. All calculations were performed using the teXsan [28] (**17**, **18**, **19**, **22**, and **25**) or the SHELXL97 [29] program (**20b**, **33** and **38**).

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## Legends

Fig. 1. *ORTEP Plots* [12] of the molecular structure of a) **17**, b) one of the two conformations of **18**, and c) **19** (50% probability ellipsoids, arbitrary numbering of the atoms)

Fig. 2. *ORTEP Plot* [12] of the molecular structure of **20b** (50% probability ellipsoids, arbitrary numbering of the atoms)

Fig. 3. *ORTEP Plot* [12] of the molecular structure of one of the two disordered orientations of **22** (50% probability ellipsoids, arbitrary numbering of the atoms)

Fig. 4. *ORTEP Plot* [12] of the molecular structure of **25** (50% probability ellipsoids, arbitrary numbering of atoms)

Fig. 5. *ORTEP Plot* [12] of the molecular structure of a) **33** and b) **38** (50% probability ellipsoids, arbitrary numbering of the atoms)

Table 1. Crystallographic Data of Compounds **17**, **18**, **19**, **22**, and **25**

	<b>17</b>	<b>18</b>
Crystallized from	CH <sub>2</sub> Cl <sub>2</sub> /hexane	CH <sub>2</sub> Cl <sub>2</sub> /AcOEt
Empirical formula	C <sub>35</sub> H <sub>26</sub> O <sub>2</sub> S <sub>2</sub>	C <sub>32</sub> H <sub>26</sub> O <sub>4</sub> S <sub>2</sub>
Formula weight [g mol <sup>-1</sup> ]	542.71	538.67
Crystal colour, habit	colorless, tablet	colorless, prism
Crystal dimensions [mm]	0.18 × 0.30 × 0.43	0.22 × 0.30 × 0.30
Temperature [K]	173(1)	298(1)
Crystal system	monoclinic	triclinic
Space group	<i>P</i> 2/ <i>c</i>	<i>P</i> <sup>-</sup> <sub>1</sub>
<i>Z</i>	4	2
Reflections for cell determination	25	6604
2 $\theta$ range for cell determination [°]	21–37	5–74
Unit cell parameters		
<i>a</i> [Å]	19.819(3)	10.2453(2)
<i>b</i> [Å]	9.031(4)	10.4024(1)
<i>c</i> [Å]	16.328(3)	13.8478(2)
$\alpha$ [°]	90	100.2566 (6)
$\beta$ [°]	106.39(1)	98.8651(6)
$\gamma$ [°]	90	106.5469 (6)
<i>V</i> [Å <sup>3</sup> ]	2804(1)	1358.90(4)
<i>D<sub>x</sub></i> [g cm <sup>-3</sup> ]	1.285	1.316
$\mu$ (MoK $\alpha$ ) [mm <sup>-1</sup> ]	0.221	0.232
Scan type	$\omega/2\theta$	$\omega$
2 $\theta$ (max) [°]	55	55
Transmission factors (min; max)	-	-
Total reflections measured	7085	22427
Symmetry independent reflections	6447	6226
Reflections used [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	4411	4633
Parameters refined	352	353
Final <i>R</i>	0.0661	0.0494
<i>wR</i>	0.0691	0.0558
Weights: <i>p</i> in $w = [\sigma^2(F_o) + (pF_o)^2]^{-1}$	0.005	0.01
Goodness of fit	2.401	2.162
Final $\Delta_{\max}/\sigma$	0.0003	0.02
$\Delta\rho$ (max; min) [e Å <sup>-3</sup> ]	0.71; -0.41	0.37; -0.26

Table 1. (continued)

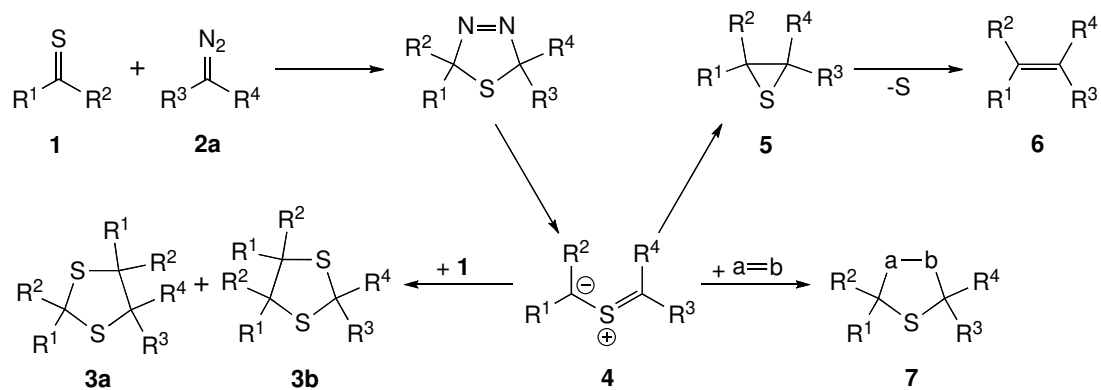
	19	22	25
Crystallized from	AcOEt	hexane/AcOEt	hexane
Empirical formula	C <sub>29</sub> H <sub>22</sub> O <sub>2</sub> S <sub>2</sub>	C <sub>20</sub> H <sub>20</sub> OS	C <sub>19</sub> H <sub>18</sub> OS
Formula weight [g mol <sup>-1</sup> ]	466.61	308.44	294.41
Crystal color, habit	colorless, prism	pale-yellow, prism	colorless, prism
Crystal dimensions [mm]	0.15 × 0.15 × 0.20	0.12 × 0.18 × 0.27	0.20 × 0.22 × 0.25
Temperature [K]	160(1)	160(1)	160(1)
Crystal system	monoclinic	monoclinic	monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>Z</i>	4	4	4
Reflections for cell determination	43672	34702	25782
2 $\theta$ range for cell determination [°]	2–60	2–55	4–60
Unit cell parameters			
<i>a</i> [Å]	14.3898(1)	9.6064(2)	8.5780(1)
<i>b</i> [Å]	9.5516(1)	10.4524(2)	12.5949(2)
<i>c</i> [Å]	17.1675(2)	16.5859(3)	13.9084(2)
$\alpha$ [°]	90	90	90
$\beta$ [°]	105.2059(4)	101.7945(7)	96.2541(7)
$\gamma$ [°]	90	90	90
<i>V</i> [Å <sup>3</sup> ]	2276.99(4)	1630.23(5)	1493.71(4)
<i>D<sub>x</sub></i> [g cm <sup>-3</sup> ]	1.361	1.257	1.309
$\mu$ (MoK $\alpha$ ) [mm <sup>-1</sup> ]	0.259	0.198	0.213
Scan type	$\phi$ and $\omega$	$\phi$ and $\omega$	$\phi$ and $\omega$
2 $\theta_{\text{(max)}}$ [°]	60	55	60
Transmission factors (min; max)	0.825; 0.964	0.861; 0.978	0.897; 0.959
Total reflections measured	59019	36152	39877
Symmetry independent reflections	6668	3734	4358
Reflections used [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	5450	2871	3384
Parameters refined	298	194	190
Final <i>R</i>	0.0398	0.0784	0.0433
<i>wR</i>	0.0466	0.0832	0.0414
Weights: <i>p</i> in <i>w</i> = [ $\sigma^2(F_o) + (pF_o)^2$ ] <sup>-1</sup>	0.01	0.007	0.005
Goodness of fit	2.302	4.726	2.484
Final $\Delta_{\text{max}}$ / $\sigma$	0.001	0.0003	0.0004
$\Delta\rho$ (max; min) [e Å <sup>-3</sup> ]	0.38; -0.25	0.85; -0.47	0.31; -0.27

Table 2. Crystallographic Data of Compounds **20b**, **33** and **38**

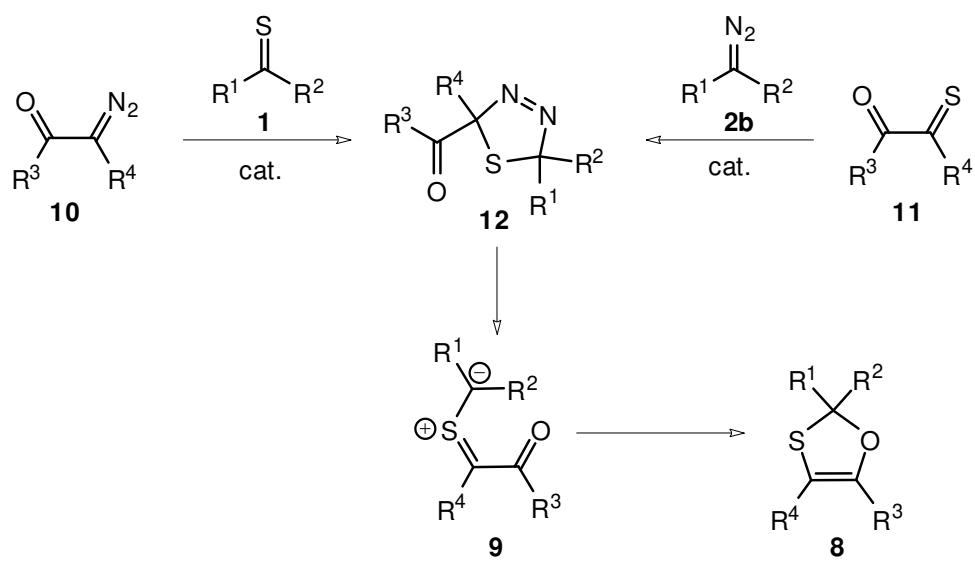
	<b>20b</b>	<b>33</b>	<b>38</b>
Crystallized from	hexane/AcOEt	hexane/CH <sub>2</sub> Cl <sub>2</sub>	hexane/CH <sub>2</sub> Cl <sub>2</sub>
Empirical formula	C <sub>22</sub> H <sub>18</sub> O <sub>2</sub> S	C <sub>23</sub> H <sub>21</sub> NS <sub>2</sub>	C <sub>16</sub> H <sub>21</sub> NS <sub>2</sub>
Formula weight [g mol <sup>-1</sup> ]	346.44	375.55	291.47
Crystal color, habit	pale yellow, prism	yellow, plate	colorless, tablet
Crystal dimensions [mm]	0.17 × 0.20 × 0.25	0.07 × 0.27 × 0.27	0.08 × 0.20 × 0.35
Temperature [K]	160(1)	160 (1)	160(1)
Crystal system	orthorhombic	orthorhombic	monoclinic
Space group	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	<i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>Z</i>	4	4	4
Reflections for cell determination	40845	21978	24601
2 $\theta$ range for cell determination [°]	4 – 55	4 – 60	4 – 60
Unit cell parameters <i>a</i> [Å]	5.5779(3)	9.2847(2)	6.4888(1)
<i>b</i> [Å]	8.1397(5)	12.7753(2)	16.6408(3)
<i>c</i> [Å]	38.894(2)	15.7321(3)	14.2958(2)
$\beta$ [°]	90	90	99.210(1)
<i>V</i> [Å <sup>3</sup> ]	1765.9(2)	1866.06(6)	1523.74(4)
<i>D<sub>x</sub></i> [g cm <sup>-3</sup> ]	1.303	1.337	1.270
$\mu$ (MoK $\alpha$ ) [mm <sup>-1</sup> ]	0.195	0.292	0.336
Scan type	$\phi$ and $\omega$	$\phi$ and $\omega$	$\phi$ and $\omega$
2 $\theta$ (max) [°]	55	60	60
Transmission factors (min; max)	0.844; 0.954	0.908; 0.982	0.895; 0.979
Total reflections measured	14153	36680	42595
Symmetry independent reflections	3957	5451	4459
Reflections with <i>I</i> > 2 $\sigma$ ( <i>I</i> )	2650	4864	3473
Reflections used in refinement	3955	5450	4457
Parameters refined	228	237	174
Final <i>R</i> ( <i>F</i> ) [ <i>I</i> > 2 $\sigma$ ( <i>I</i> ) reflections]	0.0630	0.0338	0.0404
<i>wR</i> ( <i>F</i> <sup>2</sup> ) (all data)	0.1608	0.0783	0.1104
Weighting parameters (a; b) <sup>a</sup> :	0.0649; 1.0748	0.0348; 0.4491	0.0517; 0.5980
Goodness of fit	1.040	1.053	1.040
Final $\Delta_{\max}$ / $\sigma$	0.001	0.001	0.001
$\Delta\rho$ (max; min) [e Å <sup>-3</sup> ]	0.55; -0.24	0.21; -0.31	0.31; -0.38

<sup>a</sup>)  $w^{-1} = \sigma^2 (F_o^2) + (aP)^2 + bP$  where  $P = (F_o^2 + 2F_c^2)/3$

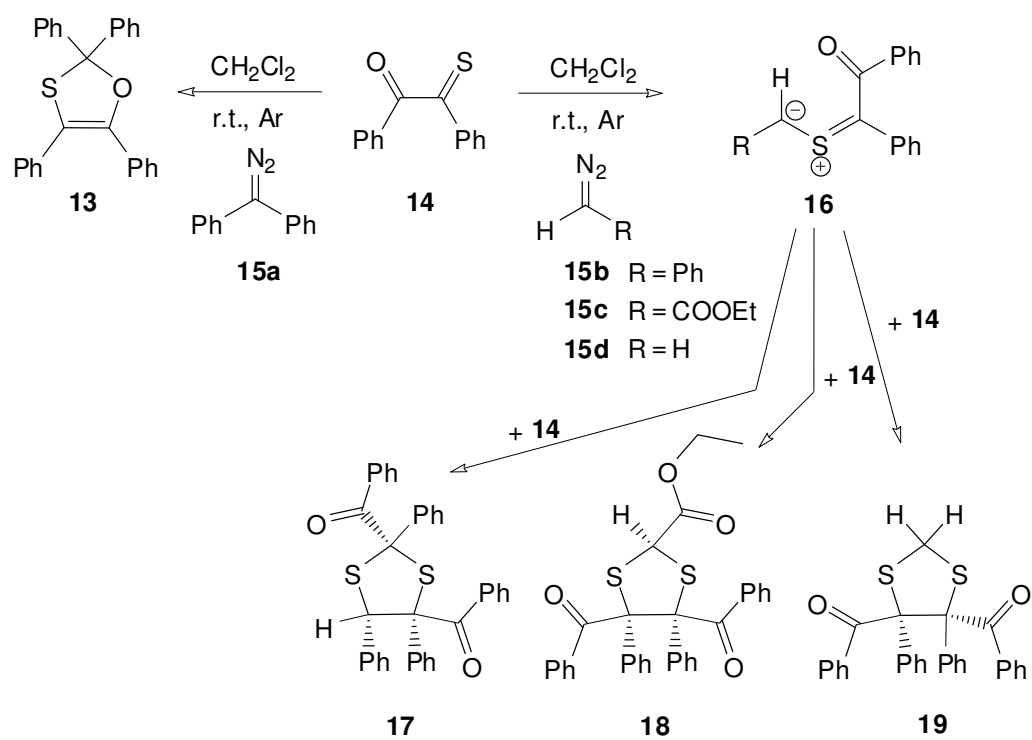
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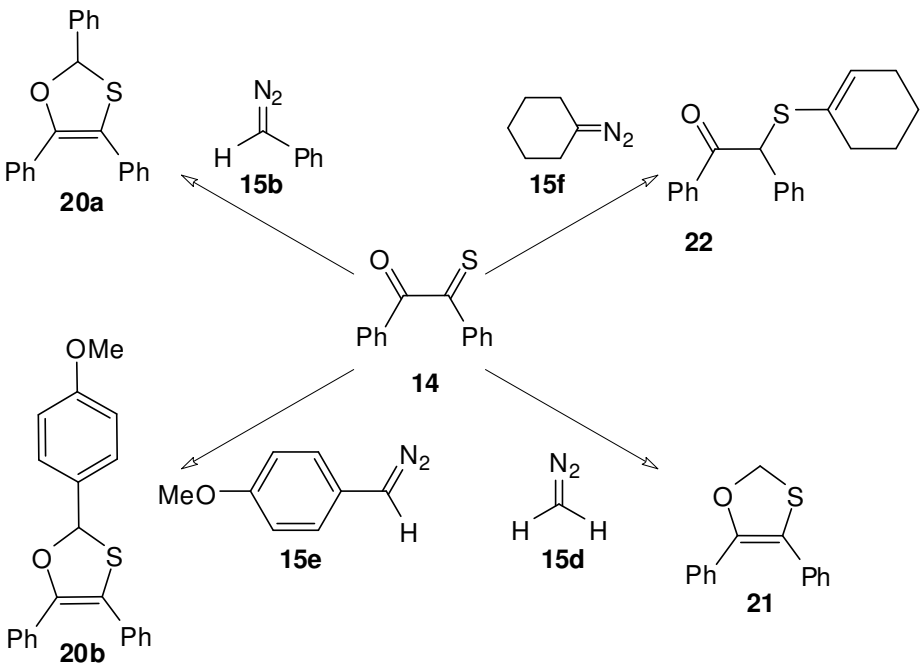
Scheme 1

*Scheme 2*

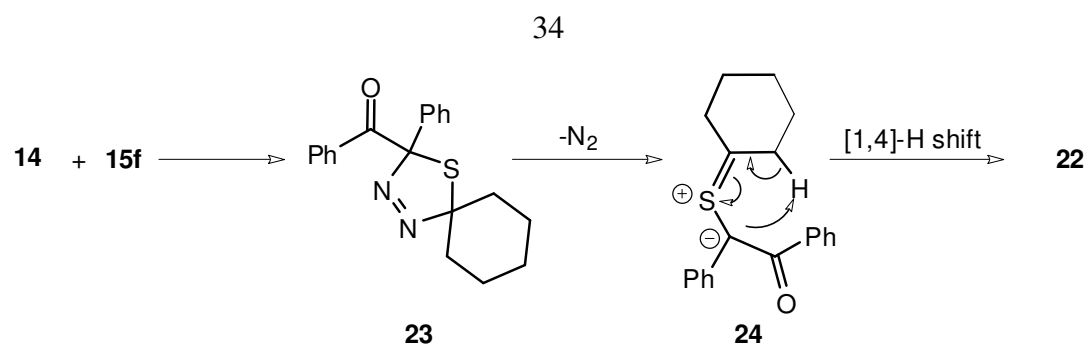




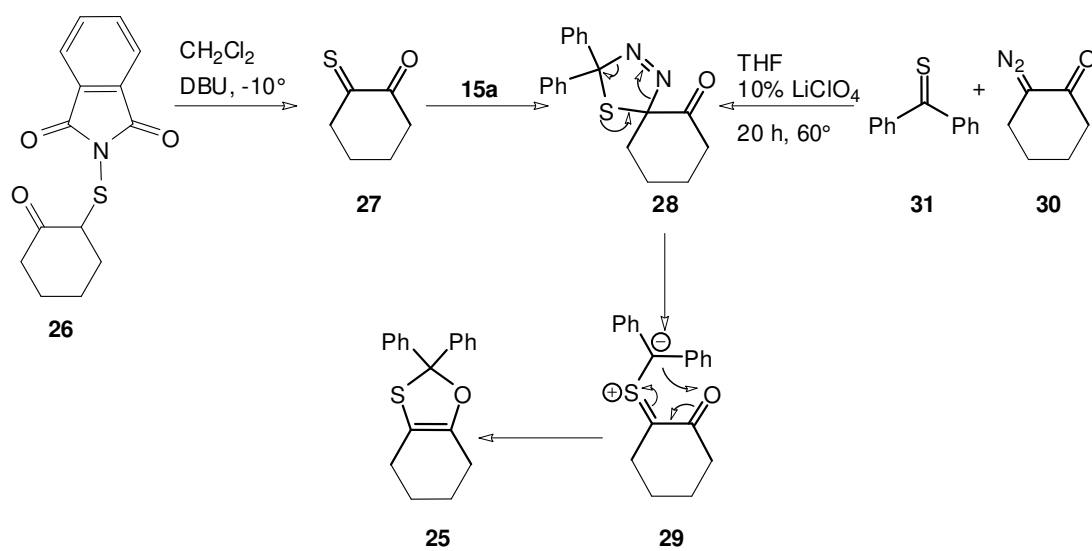
Scheme 3

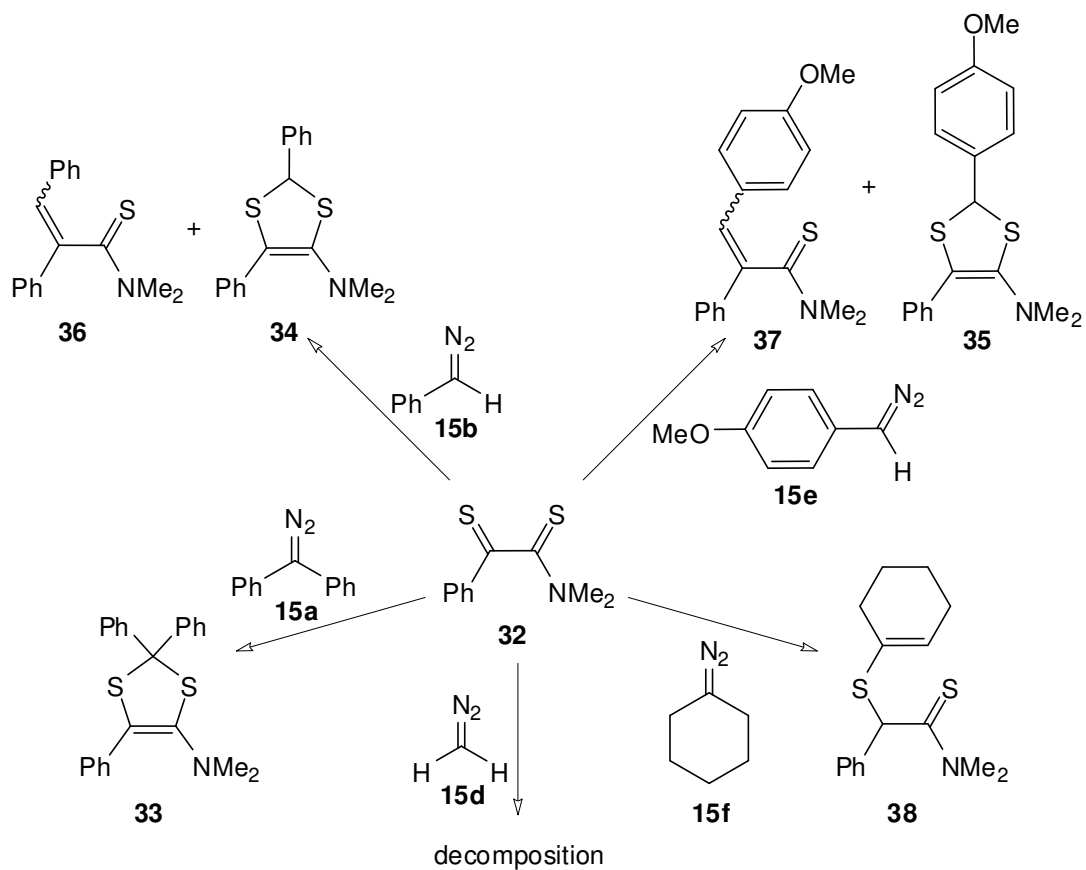


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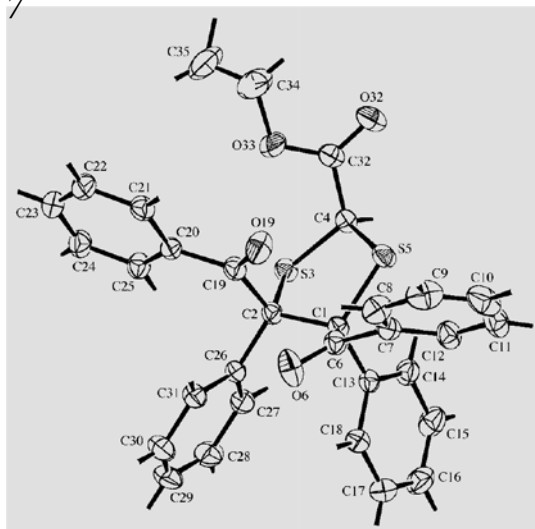
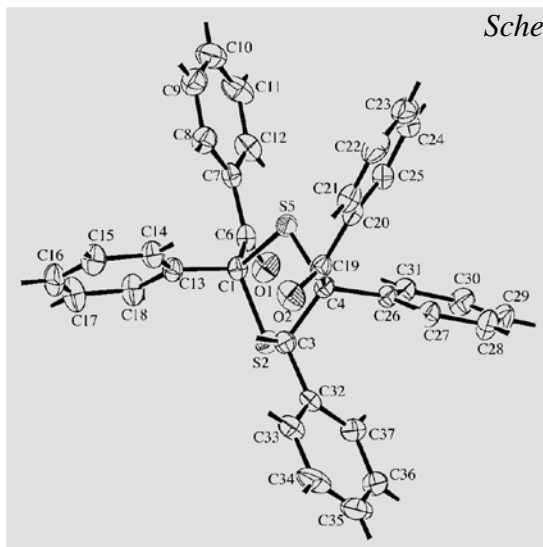


*Scheme 5*

*Scheme 6*

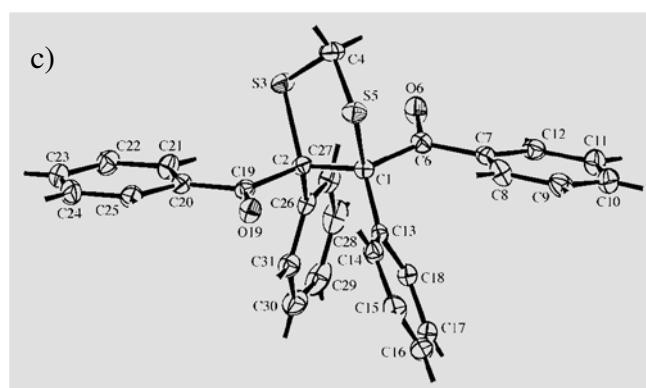


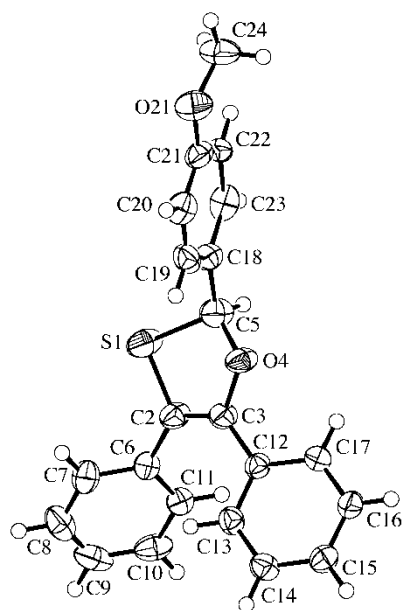
Scheme 7

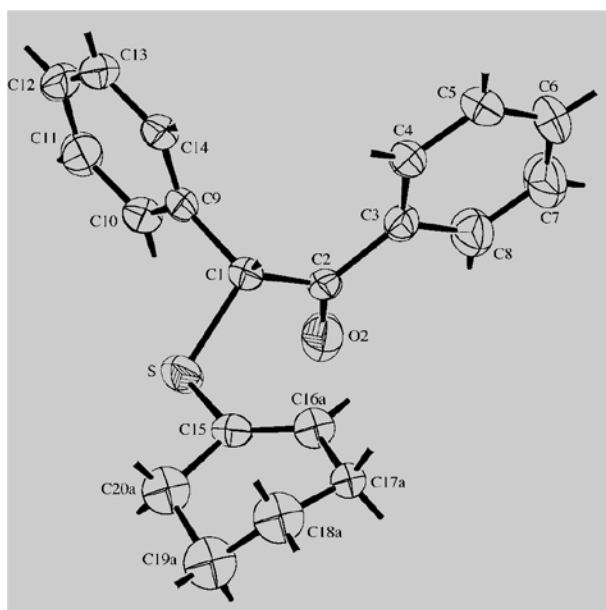


a)

b)

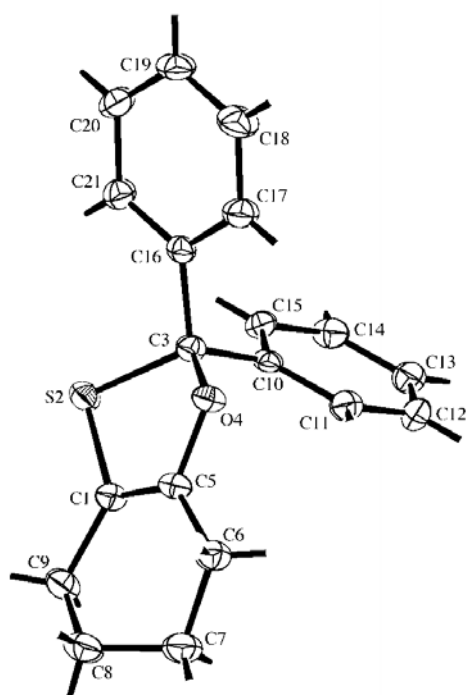
*Fig. 1.*

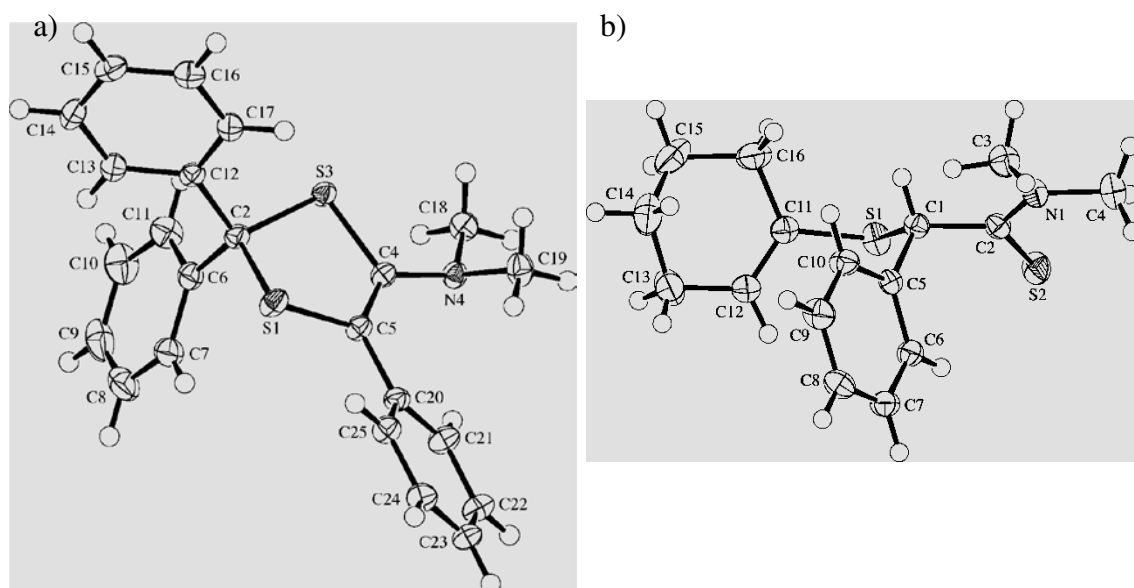
*Fig. 2.*



*Fig. 3.*



*Fig. 4.*

*Fig. 5.*

## Graphical Abstract

